Enhanced biohydrogen production by dark fermentacion using additives

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Introduction

Dark fermentation is considered as a very promising strategy for the biological generation of hydrogen. In addition, it allows a wide variety of organic waste to be used as raw material, which provides an additional advantage of waste valorization. However, dark fermentation is commonly associated with a low yield of hydrogen production compared to traditional thermochemical processes. In recent years, a strategy followed to try to overcome this barrier has been the supplementation of additives to the fermenter with the aim of intensifying the process. Additives can facilitate the microbial growth and enzymatic activity in dark fermentation, thereby leading to the enhancement of process performance. However, the application of organic and inorganic nanomaterials in biohydrogen production is still in its infancy. This work aims to shed some light on this process through the comparative study of three types of nanoparticles: zero valent iron, activated carbon and hydrochar, analyzing their effect on the dark fermentation process and hydrogen generation.

Materials and Methods

Digestate from an anaerobic reactor operating in a municipal wastewater treatment plant and glucose were used as inoculum and carbon source, respectively in the first group of test (Tier 1). Digestate from an anaerobic reactor operating in a sugar beet factory and residual effluent from this factory were used in the second group of test (Tier 2). Biogas production was measured automatically using pressure transmitters (Desin Instruments, TPR-14/N, ranging 0-1 bar) connected in the headspace of each reactor. Biogas composition was analyzed on samples collected in Tedlar bags using a Varian CP-4900 Micro-GC chromatograph with a thermal conductivity detector. Volatile fatty acids (VFA) profiles (i.e. acetic, propionic butyric, isobutyric, valeric, isovaleric, caproic and isocaproic) were determined using a gas chromatograph (GC2014, Shimadzu, Japan) equipped with a flame ionisation detector (GC-FID) while a high performance liquid chromatography equipment (HPLC1100, Agilent) with refractive index detector was use to analyse glucose and ethanol in the dark fermentation digestate. Zero valent iron nanoparticles (Smallops, 150±50nm diameter), activated carbon (Chiemivall, <0.5mm diameter) and hydrochar (Ingelia, <0.5mm diameter) were use as additives at a dose of 200 mg/L.

Glass serum bottles of 1000 mL with working volume of 500 mL were used as batch reactors. 10 g/L of glucose or sugar beet effluent and pre-incubated inoculum were taken to achieve a substrate to inoculum (S/X) ratio of 2 in the reactors. A solution of macro and micronutriens (1 mL/L) were also added but only in the Tier 1 (NH_4Cl 170 g/L, KH_2PO_4 38 g/L, $CaCl_2.2H_2O$ 8 g/L, $MgSO_4.4H_2O$ 9 g/L, $FeCl_3.4H_2O$ 2000 mg/L, $CoCl_2.6H_2O$ 2000 mg/L, $MnCl_2.4H_2O$ 500 mg/L, $CuCl_2.2H_2O$ 30 mg/L, $ZnCl_2$ 50 mg/L, H_3BO_3 50 mg/L, $(NH_4)_6Mo_7O_{24}$ 90 mg/L, $Na_2SeO_3.5H_2O$ 100 mg/L, $NiCl_2.6H_2O$ 50 mg/L, EDTA 1000 mg/L, resorcine 500 mg/L). HCl was used to create acidic conditions, bringing all tests to pH 5.5. After taking the substrate and inoculum, the reactors were flushed with nitrogen gas to purge the air remaining in the headspaces for ensuring anaerobic conditions. The reactors were hermetically sealed and placed on a shaking table in a thermostatic room at 34±1°C until exhaustion of biogas production. Each experiment was carried out in triplicate and also blank test (without substrate) were prepared to calculate the remaining endogenous biogas production of the inoculum and proceed with the corresponding results correction.

Results and main conclusions

Figure 1 shows experimental results of cumulative biogas production fitted to the modified Gompertz model for tier 1 experimentation. The additives assayed show a different degree of effectiveness on biogas production but in all the cases, the use of additives revealed to affect positively the biogas yield. Maximum biogas production is obtained by using hydrochar as an additive. In this case, 219 mL of biogas per gram of glucose are achieved. The curves corresponding to the test with activated carbon and iron nanoparticles are very similar, reaching 195 and 197 ml biogas/g glucose, respectively. Clearly, the test without the use of additive was the one that generated less biogas, with 182 ml/g glucose. Regarding the composition of the biogas, only hydrogen and carbon dioxide were detected in all cases. The non-appearance of methane reveals that no methanogenesis was generated during the process, probably due to the acidic conditions of the test with pH starting at 5.5 and evolving to more acidic pH values until the test ended. At this time, the pH reached was around 4 in all the reactors. The maximum content of

hydrogen detected in each test is shown in Table 1, highlighting the test with Fe(0) where hydrogen reached 38.4% of the biogas.

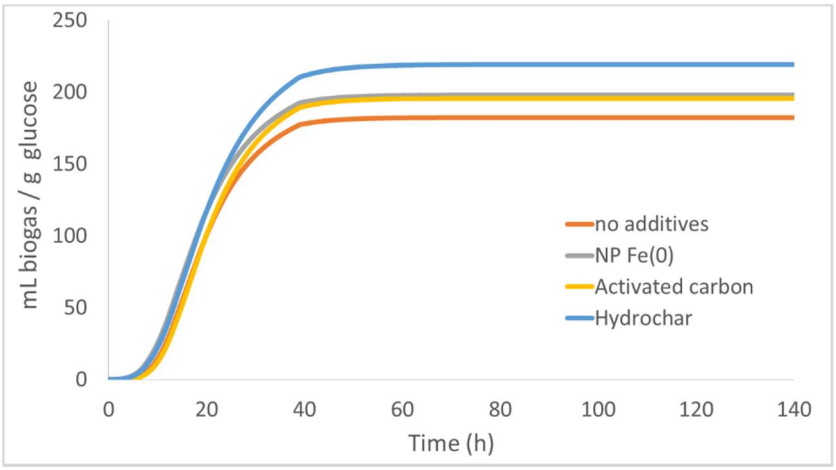

Figure 1. Effect on additives on dark fermentation. Tier 1.

Table 1. Digestate and biogas composition in Tier 1.

	No additives	NP Fe(0)	Activated carbon	Hydrochar
Biogas composition				
% H_2 max	37.4	38.4	37.7	36.5
% CH_4	0	0	0	0
Average digestate composition (SD<10% for all the measurements)				
Glucose (mg/L)	0	0	0	0
Etanol (mg/L)	16.2	12,0	10.8	5.5
Acetic acid (mg/L)	1713.7	1640.8	1650.0	1585.0
Propionic acid (mg/L)	137.8	95.5	108.1	-
Butiric acid (mg/L)	2635.6	2517.7	2704.5	2360.9
Caproic acid (mg/L)	142.2	162.3	134.5	186.5
Total VFA (mg/L)	4640.4	4416.2	4597.1	4132.3

Table 1 shows the composition of the digestate at the end of the trials in Tier 1. In all cases, it is observed how the glucose is completely consumed, generating small concentrations of ethanol and volatile fatty acids (VFA), mainly butyric, the most abundant in all trials, acetic acid and small concentrations of propionic acid in some trials. The minimum AGV concentration is observed in the test that uses hydrochar as an additive, which is consistent since it is the test in which the greatest amount of the substrate has gone to form biogas. The composition of the digestate formed opens the door for this stream to be used as a VFA source or for it to be easily degraded in a conventional anaerobic digester for biomethane production. However, if the objective of the process is to maximize hydrogen production, controlling the pH of the medium can lead to inhibiting VFA production in favor of hydrogen production.

At Tier 2, where a real wastewater stream is used instead of glucose as the carbon source, preliminary studies indicate results along the same lines as those obtained at Tier 1, with increases in biogas production greater than 2 with the use of additives. Likewise, a higher hydrogen content is also observed in the biogas generated, around 2%.

After confirming these promising results in a second round of tests, the next step will be to operate the reactors continuously, with pH adjustment to prevent the acidification of the medium from inhibiting the reaction, looking for maximizing hydrogen generation.

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